



Influence of Nucleating Agents on the Chemical Interaction of MgO-Al₂O₃-SiO₂-B₂O₃ Glass Sealants with Components of SOFCs

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The chemical interactions between different MgO-SiO₂-Al₂O₃-B₂O₃ base glass sealants and components of solid oxide fuel cells (SOFCs) were investigated. The SOFC materials considered are ZrO₂ stabilized with 8 mol % Y₂O₃ (as electrolyte and part of the anode), Ni (as part of the anode), and the oxide-dispersion-strengthened (ODS) alloy Cr5Fe1Y₂O₃ (as interconnect). Glass compositions with no nucleating agent and with ZrO₂, Cr₂O₃, or Ni as the nucleating agents were prepared. Powder mixtures of these sealants with the mentioned SOFC materials, as well as the sealant/material interfaces, were characterized by X-ray diffraction and scanning electron microscopy and energy dispersive spectroscopy in order to determine possible reaction phases and the diffusion behavior of different cations. Formation of cordierite and cristobalite as detrimental phases was detected in many of the mixtures. The formation of these phases can be suppressed if Cr₂O₃ or Ni is added to the glass as the nucleating agent. The most interesting feature of these results is the absence of the cordierite phase for all reaction powder mixtures if Cr₂O₃ is used as the nucleating agent. The sealants with Cr₂O₃ and Ni as nucleating agents formed a reaction zone at the interface with ODS, rich in Cr and Mg. A parabolic reaction rate equation describing the growth of the reaction zone thickness, the diffusion coefficient of chromium, and rate constants was evaluated.

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One of the technological problems in the development of planar solid oxide fuel cells (SOFCs) is the sealing of the stack.¹⁻⁴ Among the many glasses investigated for this purpose, aluminosilicate glass is a good candidate.

We recently investigated a large number of AO-SiO₂-Al₂O₃-B₂O₃ (A = Ba, Ca, Mg) base glasses. By detailed microstructural and structural studies and by thermal analysis, we tried to understand their crystallization and thermal expansion behavior.^{5,6} Powder mixtures and diffusion couples were investigated by us⁷ in order to elucidate the chemical interactions at the interface between sealants and other materials of SOFC at the anode side. These materials are ZrO₂ stabilized with 8 mol % Y₂O₃ (8YSZ) as the electrolyte and part of the anode, Ni as part of the anode, and the oxide-dispersion-strengthened (ODS) alloy Cr5Fe1Y₂O₃ Ductrolloy (supplied by Plansee, Reute, Austria) as interconnect. It was observed that MgO base sealants are superior to the BaO or CaO base sealants because of a higher activation energy of crystal growth thereby hindering crystallization and moderate chemical interactions at the interface. However, on interacting with different components of SOFC MgO base aluminosilicate glasses often lead to the formation of the two detrimental phases cordierite and cristobalite. The thermal expansion coefficient (TEC) of the cordierite phase is very low ($2 \times 10^{-6}/\text{K}$) compared to that of the other components of the fuel cell (FC) which is detrimental to the SOFC. Cristobalite is detrimental because it undergoes a structural transformation at 200°C involving a large volume change, which causes microcracking during cooling from the sealing temperature. The following features of the results on several magnesium aluminosilicate glasses⁷ indicate the need for further work on the development of such glasses.

1. When a particular MgO-Al₂O₃-SiO₂ base sealant and its powder mixture with nickel were annealed under similar conditions, the cordierite phase was completely suppressed in the latter.

2. When a MgO-Al₂O₃-SiO₂ base sealant with TiO₂ as nucleating agent and its powder mixture with 8YSZ were annealed under similar conditions, again the cordierite phase was only suppressed in the latter.

3. The powder mixtures of most magnesium aluminosilicate sealants with the ODS alloy or the steel Fe18Cr1Al (DIN 1.4742) did not show the lines of the cordierite phase in the X-ray diffraction (XRD) pattern. However, the presence of the cristobalite phase is seen in many cases and there seems to be a competition between the formation of cordierite and cristobalite. It may be mentioned that the diffusion of chromium into the sealant is the highest for the ODS alloy and the steel.

In view of the above noteworthy features, we chose three MgO base aluminosilicate glasses with ZrO₂, Ni, or Cr₂O₃ as the nucleating agents, respectively. The high covalent nature of the bonding of Ni and Cr ions and their high field strength values can enhance the rearrangement of the glass structure and modify the glass transition and crystallization behavior. Indeed, the glass transition temperature, T_g , and the crystallization temperature, T_c , of the two glasses with nickel and chromia as nucleating agents were the highest of all the sealants investigated so far by us.^{5,6} They also exhibited high values for the activation energy of crystal growth.⁵ For example, the values of the activation energy for the sealant without and with ZrO₂ as nucleating agent amount to 420 and 410 kJ/mol, respectively, whereas these values are 498 and 622 kJ/mol if chromia and nickel are used as nucleating agents, respectively. A high stability and compatibility have, therefore, to be expected for these two sealants. Nucleating agents play a significant role in the homogeneous nucleation and growth of phases. The growth of selected phases may be favored while that of other phases is restricted or suppressed. The choice of nucleating agents and the glass system in the present studies is based on the results obtained in our previous reports.⁵⁻⁷ We present here the results of their chemical interactions with 8YSZ (as electrolyte and part of the anode), Ni (as part of the anode) and the ODS alloy (as interconnect). Moreover, the diffusion behavior of different cations, in particular chromium, has been investigated. We also tried to explore the reasons for the suppression of undesirable phases.

Experimental

The glass compositions considered here together with their label are given in Table I. The details of the synthesis of glasses and their characterization are given elsewhere.^{5,6} The differential thermal analysis (DTA) studies were carried out using the thermal analyzer-type STA 429 supplied by Netzsch, Selb, Germany. The chemical interactions between the sealants and the components of the SOFC were investigated by annealing their powder mixtures and diffusion

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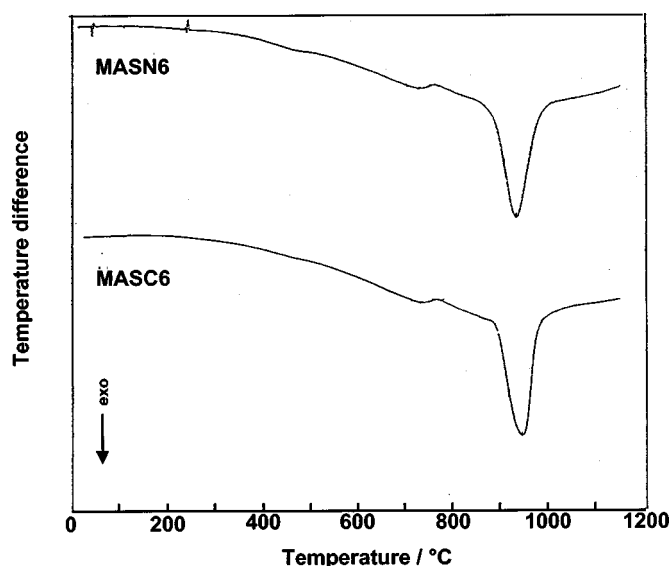
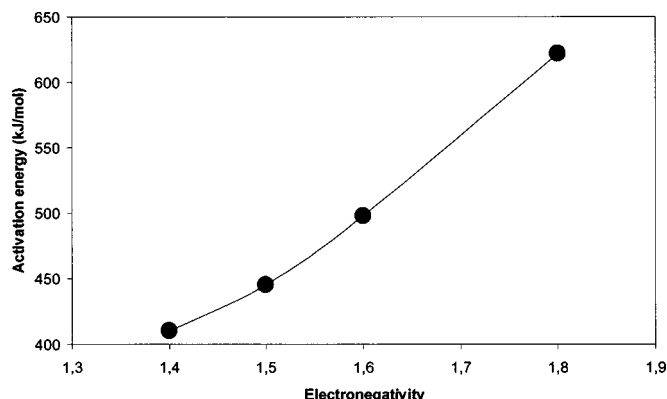
Table I. Composition of glasses investigated in mole percent with label.

Glass	MgO	SiO ₂	Al ₂ O ₃	B ₂ O ₃	ZrO ₂	Cr ₂ O ₃	Ni	Label
1	45	45	5	5				MAS
2	38	45	10	5	2			MASZ10
3	43.7	44.6	6.4	3.4			1.9	MASN6
4	46.2	42.9	6.6	3.7		0.6		MASC6

couples under ambient air. Phase analysis was conducted by XRD using Cu K α and Co K α radiation (Philips 1050, Eindhoven, The Netherlands). The chemical composition of the phases was obtained by scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX, CAMSCAN/Tracor Northern, Middleton, WI). SEM/EDX was used to determine the diffusion profile of different cations at the interface of the diffusion couples.

Results and Discussion

Figure 1 shows the DTA curves determined at a heating rate of 10 K per min for the samples MASN6 and MASC6. The DTA results of the other glasses investigated by us are reported in Ref. 5. The glass transition temperature, T_g , and the crystallization temperature, T_c , are determined by DTA. The values for T_g are 717, 723, 735, and 738°C for the glasses MAS, MASZ10, MASN6, and MASC6, respectively, whereas the T_c values are 921, 931, 939, and 946, respectively. The T_g and T_c values are significantly higher for the samples with nucleating agents. Activation energies of crystal growth were determined from the modified Kissinger equation as described in our earlier paper.⁵ The values of the activation energy are very high for the glasses containing Ni or Cr₂O₃ as the nucleating agent. The value of the activation energy for the glass MAS with no nucleating agent is 420 kJ/mol. Figure 2 shows the plot of the activation energy vs. the electronegativity for the different ions used as nucleating agents. The electronegativity which determines the bonding character seems to have a marked influence on the activation energy, though the concentration of the nucleating agents in the glass is very small. However, this is merely an observed correlation. All nucleating ions considered in this work, except Zr⁴⁺, enhance the activation energy of crystal growth. This is possibly due to the fact that these ions may act as network formers because they can

**Figure 1.** DTA thermograms determined at a heating rate of 10 K min⁻¹ for samples MASN6 and MASC6.**Figure 2.** Plot of activation energy of crystal growth vs. electronegativity of cations used as nucleating agents.

have tetrahedral coordination in addition to the higher coordination. In contrast to this, the Zr⁴⁺ ion can only have higher coordination and cannot act as a network former.

Chemical interaction in powder mixtures.—Chemical interactions were investigated by annealing powder mixtures made of the different sealants and Ni, the ODS alloy, or 8YSZ at 1000°C for 100 h. Results on the subsequent characterization of the mixtures are given in Table II. The results showed no interesting features if ZrO₂ was used as the nucleating agent. We therefore limit our further discussion to the results obtained with two sealants containing Cr₂O₃ or Ni as nucleating agents.

Figure 3 shows the XRD pattern of the powder mixtures MAS + Ni, MASN6 + Ni, and MASC6 + Ni annealed in air at 1000°C for 500 h. The pattern indicates the presence of the phases Mg₂SiO₄ (forsterite) and MgSiO₃. The cordierite phase (Mg₂Al₄Si₅O₁₈) is evident in the powder mixtures of MAS + Ni and MASN6 + Ni. The exception is the mixture MASC6 + Ni where Cr₂O₃ is used as the nucleating agent. It is very encouraging to note that the undesirable cordierite phase is completely suppressed in this powder mixture. There is another interesting observation with regard to the product phases: The lines of the MgSiO₃ product phase show high intensity for the powder mixture of MAS with Ni, whereas the lines of the Mg₂SiO₄ product phase show high intensity for the other two mixtures where nucleating agents are used. As mentioned above, our DTA results show a significantly higher T_g and T_c for the sealants with the two nucleating agents. This appears to change the crystallization kinetics and the formation of product phases in the powder mixtures. We observed a similar change in the volume fraction of the MgSiO₃ and Mg₂SiO₄ phases with varying amounts of TiO₂ as the nucleating agent in MgO-Al₂O₃-SiO₂-B₂O₃ base glasses.⁷

Figure 4 shows the XRD pattern of the powder mixtures MAS + 8YSZ, MASN6 + 8YSZ, and MASC6 + 8YSZ annealed in air at 1000°C for 100 h. The results are very similar to Fig. 3 with the exception that the additional phase ZrSiO₄ was detected in all samples as the dominant product phase. Moreover, the product phases Mg₂SiO₄ and MgSiO₃ are present in the powder mixtures. The ratio of the volume fraction of MgSiO₃ and Mg₂SiO₄ changes in a similar way to that observed in the case of the powder mixtures with nickel. The formation of the cordierite phase is suppressed in the powder mixture MASC6 + 8YSZ. Note that the suppression of the cordierite phase was also reported by us for a mixture of a MgO-Al₂O₃-SiO₂-B₂O₃ base sealant with 8YSZ, if TiO₂ was used as the nucleating agent.⁷

Figure 5 shows the XRD pattern of the powder mixtures MAS + ODS, MASN6 + ODS, and MASC6 + ODS annealed in air at 1000°C for 500 h. The XRD patterns are nearly identical. The com-

Table II. Reaction products determined by XRD in powder mixtures composed of different sealants and SOFC materials after annealing at 1000°C for 100 h in air.

Sealants	SOFC materials		
	Ni	ODS	YSZ
MAS	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, Mg_2SiO_4 , NiO , MgSiO_3	$(\text{Mg},\text{Fe})_2\text{SiO}_4$, ZrSiO_4 , MgSiO_3 , SiO_2 , $(\text{Mg},\text{Fe})(\text{Cr},\text{Al})_2\text{O}_4$	Mg_2SiO_4 , ZrSiO_4 , $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, MgSiO_3
MASZ10	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, Mg_2SiO_4 , ZrSiO_4 , NiO , MgSiO_3	$(\text{Mg},\text{Fe})_2\text{SiO}_4$, ZrSiO_4 , $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, MgSiO_3 , $(\text{Mg},\text{Fe})(\text{Cr},\text{Al})_2\text{O}_4$	Mg_2SiO_4 , ZrSiO_4 , $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, MgSiO_3
MASN6	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, Mg_2SiO_4 , $\text{Mg}_{0.4}\text{Ni}_{0.6}\text{O}$, MgSiO_3	Fe_2SiO_4 , MgSiO_3 , SiO_2 , $(\text{Mg},\text{Fe})(\text{Cr},\text{Al})_2\text{O}_4$	ZrSiO_4 , Mg_2SiO_4 , $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$
MASC6	Mg_2SiO_4 , $\text{Mg}_{0.4}\text{Ni}_{0.6}\text{O}$, MgAl_2O_4	SiO_2 , Fe_2SiO_4 , MgSiO_3 , $(\text{Mg},\text{Fe})(\text{Cr},\text{Al})_2\text{O}_4$	ZrSiO_4 , Mg_2SiO_4 , MgSiO_3 , MgAl_2O_4

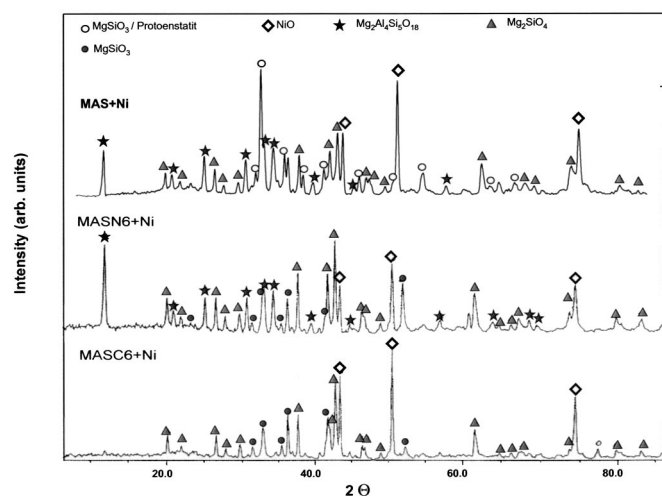
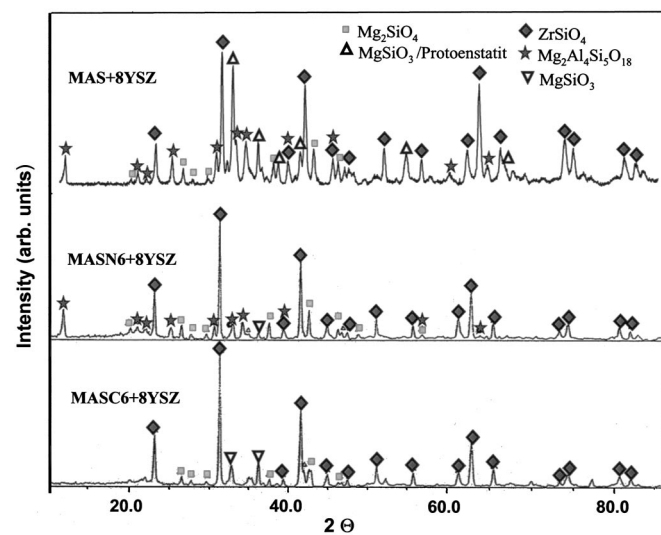
mon phases are MgSiO_3 , spinel, and cristobalite. It is interesting to note that the cordierite phase is absent in the powder mixtures. However, another detrimental phase, cristobalite, was detected. It may be recalled that the cordierite phase was detected when the sealant MAS was annealed at 1000°C for 1000 h, while the cristobalite phase was absent.⁵ There seems to be some competition between the formation of cordierite and cristobalite as discussed in our previous paper.⁷

The most encouraging and interesting result is the complete absence of cordierite phase in all reaction mixtures of sealant MASC6 with the three SOFC materials. This is discussed in the following.

In our previous paper,⁷ we observed the suppression of the cordierite phase in some reaction mixtures if TiO_2 was used as nucleating agent. This could be understood in terms of phase separation induced by TiO_2 . In the case of chromium oxide as the nucleating agent, chromium can exist in the glass as 3+ and 6+ states if the glass is melted under oxidizing conditions. The relative proportion of these ions depends on the melting conditions or the other cations present in the glass.⁸ Cr^{6+} represents an ion with a very high field strength value of 2.40 compared to those of Ti^{4+} and Ni^{2+} , which amount to 1.25 and 0.61, respectively. Moreover, it normally occupies an interstitial position due to the small ionic radius of ~ 0.052 nm, which exerts a marked ordering effect upon the oxygen ions surrounding it. Under these circumstances, a chromium-rich phase can separate out from this glass.⁸ This is supported by our studies on the diffusion couples that are reported in the following section. The

phase separation is presumably responsible for the restriction in the growth of cordierite phase in the powder mixtures. The T_g and T_c of this glass is the highest of all the sealants investigated by us.^{5,6} Moreover, the activation energy of crystal growth is very high (498 kJ/mol). These observations suggest that the crystallization kinetics of this glass is different from the other glasses. It may be noted that the difference in the glass compositions seems to be too small to be attributed to thermodynamic instability of the cordierite phase.

Investigation of diffusion couples.—A detailed investigation of the diffusion couples MASN6/ODS and MASC6/ODS was carried out after annealing at 1000°C for different time periods to study the diffusion behavior of different cations across the interfaces. Figure 6 shows the SEM micrographs of these two diffusion couples annealed for 22 h and 100 h, respectively, as typical examples. Figure 7 allows the comparison of the diffusion profiles of different cations in the two diffusion couples. The reaction zone grows faster if Ni is used as the nucleating agent in the sealant and shows major concentrations of Cr and Mg. The diffusion of Si in the reaction zone is essentially negligible. The reasons for the formation of a Cr-Mg-rich zone are discussed in the previous section as well as in our previous paper.⁷ The reaction kinetics between Cr and Mg ion is rapid and this favors the formation of the spinel phase. In such a situation, the formation of the cordierite phase is inhibited. At the reaction tem-

**Figure 3.** XRD pattern of powder mixtures of (a) MAS + Ni, (b) MASN6 + Ni, and (c) MASC6 + Ni after annealing in air at 1000°C for 500 h.**Figure 4.** XRD pattern of powder mixtures of (a) MAS + 8YSZ, (b) MASN6 + 8YSZ, and (c) MASC6 + 8YSZ after annealing in air at 1000°C for 500 h.

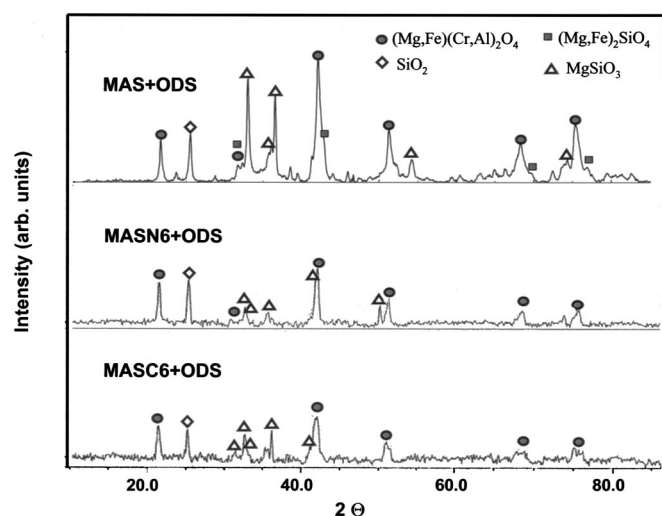
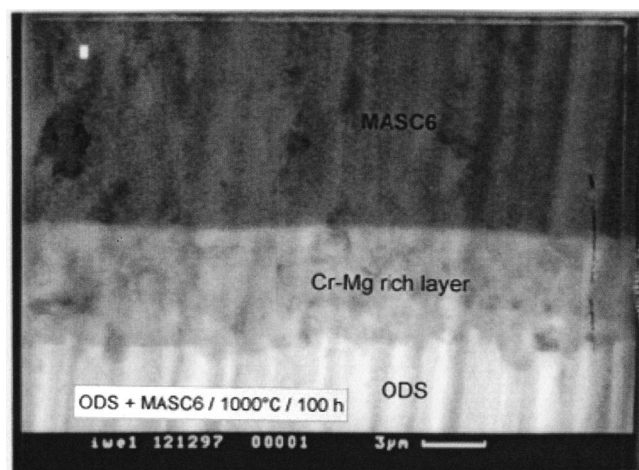
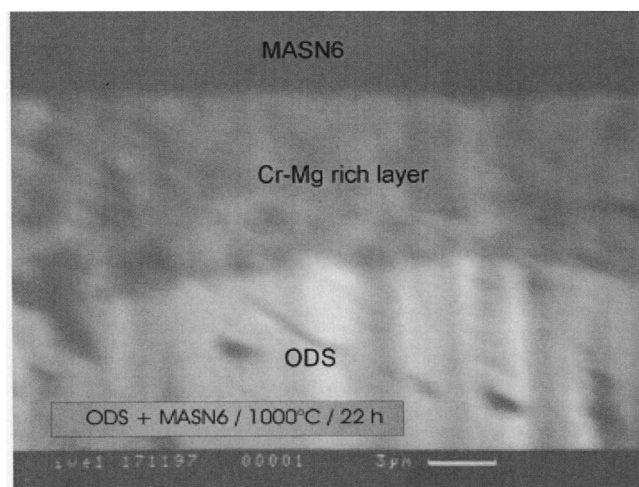


Figure 5. XRD pattern of powder mixtures of (a) MAS + ODS, (b) MASN6 + ODS, and (c) MASC6 + ODS after annealing in air at 1000°C for 500 h.

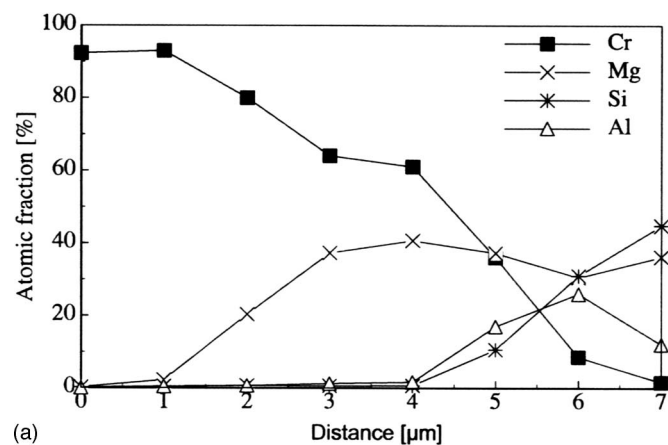


(a)

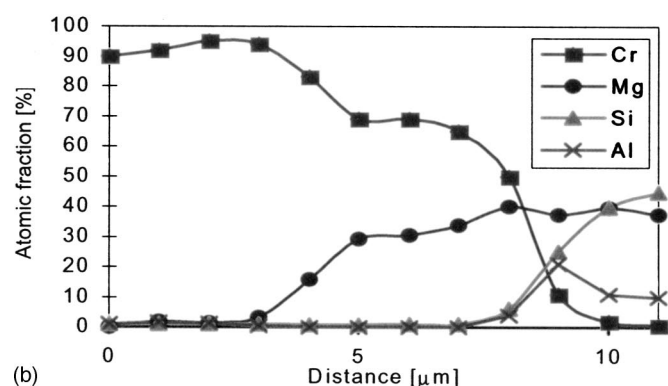


(b)

Figure 6. Typical SEM micrographs of the interface of (a) MASC6 + ODS, and (b) MASN6 + ODS after annealing at 1000°C for 100 h or 22 h, respectively.



(a)



(b)

Figure 7. Typical diffusion profile of different cations at the interface of (a) MASN6 + ODS, and (b) MASN6 + ODS after annealing at 1000°C for 100 h or 22 h, respectively.

perature and in the reaction zone, mobile oxygen ions are always available for the oxidation of chromium and formation of spinel phase, thus maintaining the charge neutrality.

Figure 8 shows the square of the interdiffusion layer thickness, X^2 , plotted vs. the diffusion time, t , for the interfaces of the sealants MASN6 and MASC6 with the ODS alloy. The thickness of the interdiffusion layer initially increases parabolically with time and then becomes constant in practical terms after 20 h. The linear relation between X^2 and t observed in the initial portion of the curves strongly suggests that the formation of the interdiffusion layer is

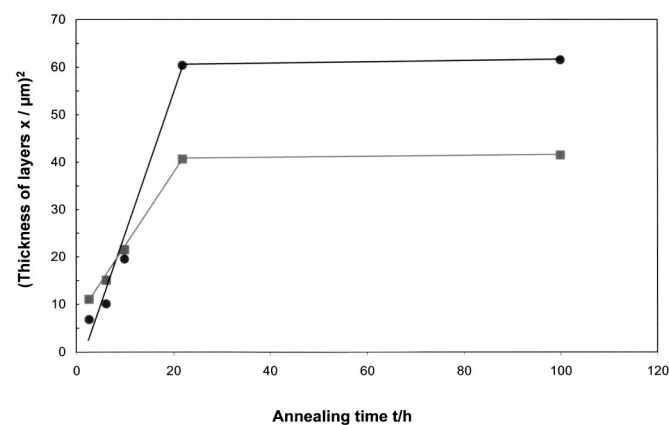


Figure 8. Plot of square of thickness of reaction layer, X^2 , vs. time, t , for the diffusion couples (●) MASN6/ODS and (■) MASC6/ODS after annealing at 1000°C for different time periods.

Table III. Diffusion coefficients, D , of chromium determined from the diffusion couples of MASN6/ODS and MASC6/ODS after annealing at 1000°C for different time periods Δt . X is the diffusion distance (see text).

Diffusion couple	$\Delta t/h$	$X/\mu m$	$D/(10^{12} \text{ cm}^2/\text{s})$	Mean value of $D/(10^{12} \text{ cm}^2/\text{s})$
MASN6/ODS	2	4	2.7	1.5
	6	7	2.8	
	10	7	1.7	
	22	9	1.3	
	100	9	0.3	
	1100	36	0.4	
MASC6/ODS	2	3	3.1	1.9
	6	8	4.1	
	10	8	2.5	
	20	9	1.6	
	100	6	0.14	
	1100	10	0.01	

controlled by the diffusion of ions. By using least squares computations, the linear portions in Fig. 8 can be described by the parabolic reaction rate equation⁹

$$X^2 = kt \quad [1]$$

where k is the parabolic growth rate constant. The parabolic growth rate constants evaluated are 3.7×10^{-12} and $8.0 \times 10^{-12} \text{ cm}^2/\text{s}$ for the sealants MASC6 and MASN6, respectively. The saturation behavior observed after 20 h can be understood in terms of the changing composition of the sealants. With time, the reaction layer becomes richer in chromium (from the ODS alloy) and in magnesium (from the sealant). Consequently, the concentration of magnesium in the sealant and of chromium in the ODS alloy is depleted. The depletion of magnesium (MgO is a network modifier) from the sealant can raise the viscosity of the sealant and distort the open SiO_4 tetrahedra. This can restrict the movement of ions, which may result in the observed slowing down of the growth of the reaction zone.

Chemical diffusion coefficients were determined from the diffusion profile of the various cations by using the relation¹⁰

$$C(x,t)/C_0 = 1 - \text{erf}[x/2(Dt)^{1/2}] \quad [2]$$

where $C(x,t)$ is the concentration of ions measured at the distance, x , from the surface of the ODS alloy for a given time period t . C_0 is the initial concentration of ions and D the diffusion coefficient. The term erf denotes the error function and its values can be obtained from the literature.¹⁰ The diffusion distance for the MASN6/ODS couple was determined between the nominal Cr concentration in the ODS alloy down to 1 atom % of Cr in the sealant. For the diffusion couple MASC6/ODS, the distance was determined down to 2.5

atom % of Cr in the sealant because the sealant contained Cr_2O_3 . The diffusion coefficients were determined by annealing the diffusion couples at 1000°C for different time periods (Table III). The average chemical diffusion coefficients for chromium at 1000°C for the diffusion couples MASC6/ODS and MASN6/ODS resulted as $1.9 \times 10^{-12} \text{ cm}^2/\text{s}$ and $1.5 \times 10^{-12} \text{ cm}^2/\text{s}$, respectively. This is in good agreement with the value of the diffusion coefficient of Cr, $1.2 \times 10^{-12} \text{ cm}^2/\text{s}$, which was obtained after annealing a diffusion couple between the ODS alloy and a sealant containing TiO_2 as nucleating agent at 1000°C for 50 h.⁷

Conclusions

The chemical interaction between $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ base glass sealants containing Cr_2O_3 , Ni, or ZrO_2 as nucleating agents with 8YSZ, Ni, and the ODS alloy were investigated. The most encouraging result is the complete absence of the cordierite phase in all powder mixtures composed of the sealant with Cr_2O_3 as the nucleating agent and the FC materials. We attribute this to the high values of T_g and T_c , and the activation energy of crystal growth if Cr_2O_3 (0.6 mol %) is used as the nucleating agent. Moreover, chromium seems to have a thermodynamic affinity to magnesium which favors spinel formation and suppresses the formation of the cordierite phase in many powder mixtures. Chemical diffusion coefficients for the chromium cation were determined from the diffusion profile and compared with literature values. The thickness of the interdiffusion layer initially increases parabolically with time and then becomes constant in practical terms after 20 h. The parabolic growth suggests that the formation of the interdiffusion layer is controlled by the diffusion of ions. The saturation behavior is understood in terms of the changing composition of components with time.

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